Homogenous Catalysis V. Hydrosilylation of Dienes with Octacarbonyldicobalt(0)

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A.J. Cornish, M.F. Lappert and T. A. Nile, (1977) "Hydrosilylation of Dienes with Octacarbonyldicobalt", *J. Organometallic Chem., 136(1),* 73.

Summary:

The room temperature hydrosilylation of linear 1,3-dienes and 1,3- or 1,4- cyclohexadienes using octacarbonyldicobalt(0) is described. Both cyclic dimers yield regiospecifically 2-cyclohexenylsilanes. The 2,3-dimethyl-1,3-butadiene (DMBD)/$HSi(OSiMe_3)_2Me$ system has been investigated in particular detail, with variation of the concentrations of reactants or catalyst, temperature, solvent, or added ligands. The effect of these changes upon (a) total yield of silylated products and (b) relative proportions of the isomeric 1,2- or 1,4-adducts of silane to diene (diene/$HSiX_3$) and of the bis-silylated adduct (diene/2 $HSiX_3$), are assessed. π-Allylcobalt intermediates are suggested.

Article:

Introduction

Octacarbonyldicobalt(0) is an active catalyst for the hydrosilylation of olefins [2-4], *α,β*-unsaturated nitriles [3], and alkynes [5]. We now report on our studies on the hydrosilylation of 1,3-dienes using octacarbonyldicobalt(0) as a catalyst. Our initial aim was to investigate the factors influencing 1,2- and 1,4-addition, as the use of octacarbonyldicobalt(0) has been reported to give high yields of 1,2-adducts [6]. We find that 1,2- and 1,4-adducts (I and II) are formed for a variety of slimes and dienes, using mild reaction conditions (20°C for 8 h), and that in certain cases significant amounts of di-adducts (III), resulting from the addition of two molecules of silane to one molecule of diene, are also formed (eq. 1). Similar formation of di-adducts has been reported for cobalt-based

$$CH_2{=}C(R)C(R'){=}CH_2 + HSiX_3 \rightarrow$$
$$CH_2{=}C(R)C(R')HCH_2SiX_3 + MeC(R){=}C(R')CH_2SiX_3 \quad (1)$$
(I) (II)
$$+ X_3SiCH_2CH(R)CH(R')CH_2SiX_3$$
(III)

(Ia: R = R′ = Me, $X_3 = (OSiMe_3)_2Me$; Ib: R = R′ = Me, $X_3 = Et_2Me$; Ic: R = H, R′ = Me, $X_3 = (OSiMe_3)_2Me$. IIa: R = R′ = Me, $X_3 = (OSiMe_3)_2Me$; IIb: R = R′ = Me, $X_3 = Et_2Me$; IIc: R = H, R′ = Me, $X_3 = (OSiMe_3)_2Me$. III: R = R′ = Me, $X_3 = (OSiMe_3)_2Me$)

Ziegler systems [7]. The hydrosilylation of 2,3-dimethyl-1,3-butadiene (DMBD), by bis(trimethylsiloxy) methylsilane was investigated in detail.

Results

The hydrosilylation of linear 1,3-dienes and cyclic 1,3- or 1,4-dienes gives, in a mildly exothermic reaction at room temperature, good yields of adducts. 1,5- Cyclooctadiene and norbornadiene gave no adducts. The results are summarised in Table 1.

The hydrosilylation of DMBD by bis(trimethylsiloxy)methylsilane was studied as a function of the reactant and catalyst proportions, the reaction temperature, the addition of ligands, and the reaction solvent.

TABLE 1

HYDROSILYLATION OF DIENES AT 20°C [a]

Diene	Silane	Time (h)	Yield [b] (%)	Products (Relative yields %)
2,3-Dimethyl-1,3-butadiene	$HSiEtMe_2$	8	82	32 1,2-adduct (I) 46 1,4-adduct (II) 4 di-adduct (III)
2,3-Dimethyl-1,3-butadiene	$HSi(OSiMe_3)_2Me$	8	80	14 1,2-adduct (I) 15 1,4-adduct (II) 51 di-adduct (III)
2-Methyl-1,3-butadiene	$HSi(OSiMe_3)_2Me$	12	55	24 1,2-adduct (I) 31 1,4-adduct (II)
1,3-Cyclohexadiene	$HSi(OEt)_3$	12	88	1/1 adduct (IV)
1,4-Cyclohexadiene	$HSi(OEt)_3$	12	48	1/1 adduct (IV)
1,3-Cyclo-octadiene	$HSi(OEt)_3$	8	82	1/1 adduct (see Table 10)
1,3-Cyclo-octadiene	$HSiEt_3$	12	65	1/1 adduct (see (see Table 10)
1,5-Cyclo-octadiene	$HSi(OEt)_3$	15	0	—
1,5-Cyclo-octadiene	$HSiEt_3$	18	0	—
Norbornadiene	$HSi(OEt)_3$	24	0	Some polymerisation occurs

[a] Diene, 8.8 mmol; silane, 4.4 mmol; $[Co_2(CO)_8]$, 6.8×10^{-2} mmol added at 20°C; stirred at 20°C. [b] Based on silane; calculated by quantitative GLC.

Variation of the diene/silane ratio

The hydrosilylation of DMBD by $HSi(OSiMe_3)_2Me$ is sensitive to the variation of the ratio of diene to silane (Table 2). The overall yield, with respect to silane, remains reasonably constant, but the amount of mono-adduct formed increases, with increase in the diene/silane ratio. The ratio of 1,2-I to 1,4-II mono-adduct remains at approximately 50/50. As the volume of the solution is not constant, an increase in the diene/silane ratio, by increasing the volume of diene used, also causes a decrease in the concentration (mol/litre) of the catalyst.

TABLE 2

HYDROSILYLATION OF DMBD CATALYSED BY $[Co_2(CO)_8]$; VARIATION OF THE DMBD/$HSi(OSiMe_3)_2Me$ RATIO [a]

Molar ratio of DMBD/$HSi(OSiMe_3)_2Me$	Yield (%)	Ratio of silane used in forming mono-adducts to that used in di-adduct formation	Ratio of 1,2- to 1,4-mono-adducts
1	76	27/73	44/56
2	80	36/64	52/48
4	80	47/53	53/47
10	72	71/29	50/50

[a] Silane 4.4 mmol; $[Co_2(CO)_8]$, 6.8×10^{-2} mmol; stirred at 20°C for 8 h. [b] Based on silane; calculated by quantitative GLC.

Variation of the $[Co_2(CO)_8]/[His(OSiMe_3)_2Me]$ ratio

Changing the amount of catalyst (mol %, relative to silane) causes minor variations in yield and product distribution (Table 3). An increase in the amount of catalyst causes a slight increase in the amount of mono-adduct (I + II) formed, and in the proportion of 1,2-mono-adduct I.

TABLE 3

HYDROSILYLATION OF DMBD CATALYSED BY $[Co_2(CO)_8]$; VARIATION OF THE CATALYST/SILANE RATIO [a]

Mole (%) $[Co_2(CO)_8]$ [b]	Yield (%) [c]	Ratio of silane used in forming mono-adducts to that used in di-adduct formation	Ratio of 1,2- to 1,4-monoadducts
1	84	29/71	50/50
2	80	36/64	52/48

[a] Silane, 4.4 mmol; DMBD, 8.8 mmol; 20°C for 8 h. [b] With respect to silane. [c] Based on silane; calculated by quantitative GLC.

Effect of temperature

An increase in temperature causes similar changes to an increase in the amount of catalyst (Table 4). The formation of mono-adducts (I + II) is favoured by higher temperatures. The proportion of 1,2-mono-adduct I also shows a slight increase with temperature. The drop in yield at 80°C, has precedent, as [$Co_2(CO)_8$] becomes inactive for the hydrosilylation of olefins above 60°C [3].

TABLE 4

HYDROSILYLATION OF DMBD CATALYSED BY [$Co_2(CO)_8$]: VARIATION OF THE TEMPERATURE [a]

Temperature (°C) [b]	Yield (%) [c]	Ratio of silane used in forming mono-adducts to that used in di-adduct formation	Ratio of 1,2- to 1,4-monoadducts
20	84	32/68	50/50
60	93	41/59	53/47
80	69	54/46	60/40

[a] DMBD, 8.8 mmol; $HSi(OSiMe_3)_2Me$, 4.4 mmol; [$Co_2(CO)_8$], 6.8×10^{-2} mmol. [b] Oil bath temperature; held at this temperature for 4 h. [c] Based on silane; calculated by quantitative GLC.

Effect of solvent

The addition of n-hexane or dichloromethane causes little change in yield or product distribution (Table 5), but use of a more polar solvent such as diethyl ether, dioxan, or THF, causes a progressive increase in the amount of mono-adduct (I + II) formed, until with THF III is no longer formed. These polar solvents also cause an increase in the proportion of 1,4-mono-adduct II formed (Table 5).

TABLE 5

HYDROSILYLATION OF DMBD CATALYSED BY [$Co_2(CO)_8$]: VARIATION OF SOLVENT [a]

Solvent [b]	Yield (%) [c]	Ratio of silane used in forming mono-adducts to that used in di-adduct formation	Ratio of 1,2- to 1,4-monoadducts
None	80	36/64	52/48
n-Hexane	76	35/65	50/50
Dichloromethane	86	34/66	50/50
Diethyl ether	72	49/51	44/56
Dioxan	76	78/32	20/80
THF	75	100/0	35/65

[a] DMBD, 8.8 mmol; $HSi(OSiMe_3)_2Me$, 4.4 mmol; [$Co_2(CO)_8$], 6.8×10^{-2} mmol; 8 h at 20°C. [b] Solvent, 1 ml. [c] Based on silane; calculated by quantitative GLC.

Addition of ligands

Attempts to stabilise the catalyst system at higher temperatures (80°C) by the addition of various tertiary phosphines or phosphites were moderately successful (Table 6). Soft ligands such as triphenylphosphine or triphenyl phosphite cause an increase in yield, whereas with the more basic dimethylphenylphosphine the yield is not significantly changed. All the ligands added cause the amount of mono-adduct (I + II) to increase. The ratio of 1,2-I to 1,4-II mono-adduct is almost invariant with ligand (Table 6).

Cyclic dienes

Octacarbonyldicobalt(0) is an active catalyst for the hydrosilylation of conjugated cyclic dienes resulting in the product of 1,4-addition only (e.g., eq. 2). Furthermore, the non-conjugated 1,4-cyclohexadiene gives the same product (IV). This feature was noted for the case of $Ni(acac)_2/Al(OEt)Et_2/PPh_3$ as catalyst [1]. Hydrosilylation does not occur with 1,5-cyclooctadiene and polymerisation is found with [2,2,1]-bicyclo-1,5-heptadiene (norbornadiene) in the presence of the normal reaction mixture, but 1,3-cyclooctadiene is hydrosilylated to give the allylic products 2-cyclooctenyl-SiX_3 (X = Et or EtO) identified by ^1H NMR (Table 10). Di-adducts (i.e., diene/2 $HSiX_3$) or 1,2-adducts (i.e., the 3-cyclohexenylsilane isomer of IV) are not observed.

(2)

(IV)

(X = Et or EtO)

Discussion and mechanism

I. The hydrosilylation of linear dienes

(a) Formation of mono-adducts (1/1 diene/silane adducts). The formation of the mono-adducts (I + II) can be explained (Fig. 1) in terms of a mechanism analogous to that proposed for the hydrosilylation of olefins by $[Co_2(CO)_8]$ [8]. The first step is the interaction between the DMBD and the catalytic species, presumed to be hydridotricarbonylcobalt(I), by analogy to the active species postulated for hydroformylation [9-11] and hydrogenation [12] reactions. The replacement of the carbonyls in the $[HCo(CO)_3]$ intermediate by DMBD, leading to a catalytic species such as [HCo(CO)DMBD], is also a possibility, but has not been included in Fig. 1 for the sake of simplicity. DMBD is known to react with $[Co_2(CO)_8]$ at reflux giving $[(\pi\text{-DMBD})CO_2(CO)_6]$ and $[(\pi\text{-DMBD})Co(CO)_2]_2$ [13].

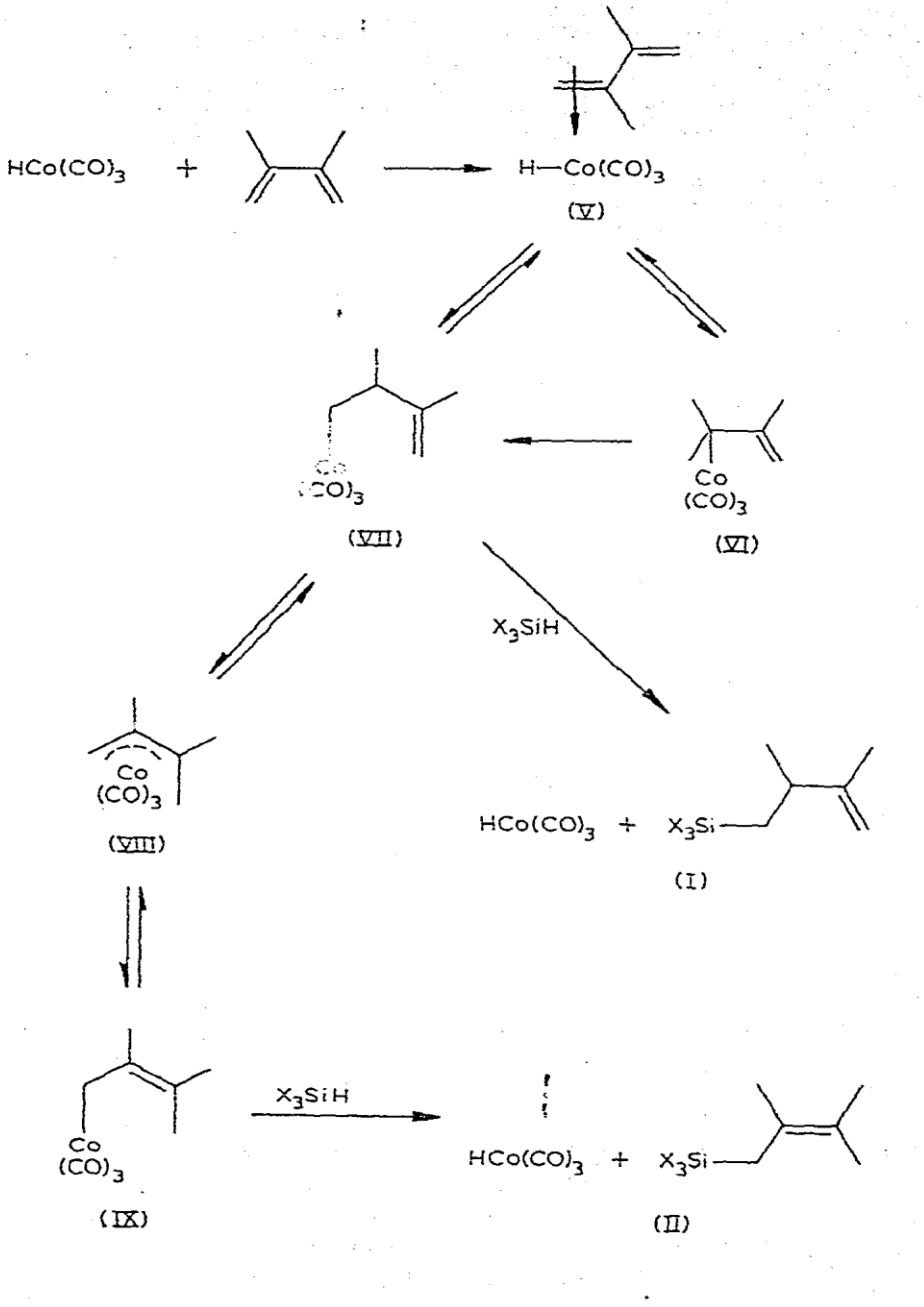


Fig. 1. Proposed mechanism for mono-adduct formation from DMBD.

The initial product is thus a π-olefin complex V. It has been concluded that a straight chain 1-alkene is approximately neutral towards hydridotetracarbonylcobalt(I) [11], and thus both Markownikoff and anti-Markownikoff addition of the cobalt hydride might be expected. Markownikoff addition of the cobalt hydride leads to the tertiary alkyl VI; such an addition is not favoured on steric grounds and the tertiary alkyl, if formed, would be expected to rearrange rapidly to the primary alkyl VII, which is the product of anti-Markownikoff

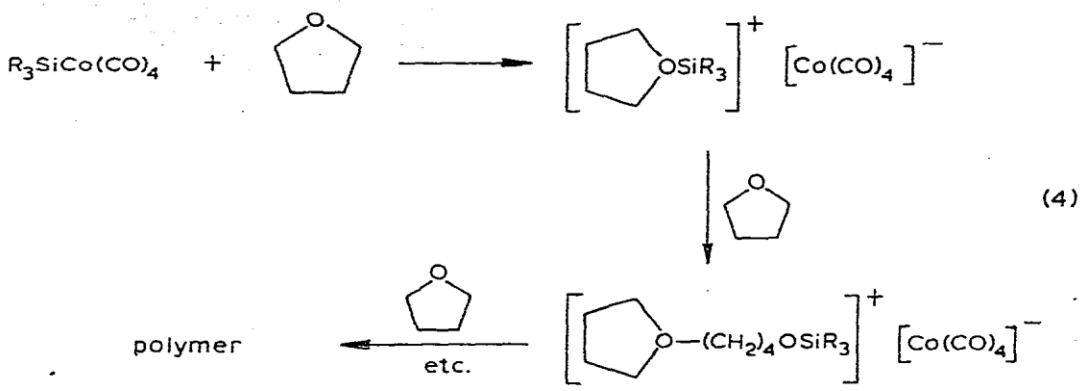
addition. Consistent with this, no hydrosilylation adducts derived directly from VI, i.e., $CH_2=C(Me)C(Me)_2SiX_3$, are isolated from the reaction mixtures.

Reaction of the primary alkyl VII with silane leads to the 1,2-adduct I, $CH_2=C(Me)CH(Me)SiX_3$, and regenerates the hydridotricarbonylcobalt(I). The primary alkyl VII may rearrange, via the π-allyl intermediate VIII to give the primary alkyl IX. The reaction of IX with silane leads to the 1,4-adduct II, $Me_2C=C(Me)CH_2SiX_3$.

The original intention was to study the factors influencing 1,2- and 1,4-addition. However, the ratio of 1,2- to 1,4-mono-adducts, I/II, is constant at 55/45 (±5%) and independent of temperature, ligand, or solvent (except with THF or dioxan). The small variations in ratio are within experimental error. This suggests either that the two mechanisms leading to the products are affected identically by changes in conditions, or that isomerisation of the products occurs (I⇌II), leading to the formation of the two isomers in thermodynamic proportions. The latter seems a more likely explanation in view of the effectiveness of $[Co_2(CO)_8]$ in the isomerisation of olefins [11,14].

The two cases where the ratio of the 1,2- to 1,4-adducts is significantly different are when THF or dioxan is the solvent. Polar compounds are known to cause the disproportionation of $[Co_2(CO)_8]$ [15], as exemplified in eq. 3 [16]. THF is polymerised by $[Co_2(CO)_8]$ in the presence of silanes [17], and a cationic mechanism was proposed.

$$3[Co_2(CO)_8] \xrightarrow{THF} [Co(THF)_6][Co(CO)_4]_2 + 8\,CO \qquad (3)$$



Thus reactions of $[Co_2(CO)_8]$ in the presence of polar solvents, especially cyclic ethers, are unusual. No polymerisation of THF or dioxan was observed during the hydrosilylation of DMBD. Replacement of the carbonyl ligands by THF is presumably involved, but the exact nature of this on the product distribution is obscure.

(b) Formation of di-adduct (112 diene/silane adduct). A possible mechanism for the formation of the di-adduct III is illustrated in Fig. 2. Steps 1, 2, 3 and 8 represent the catalytic cycle already proposed for the production of the mono-adduct I (Fig. 1). The formation of the alkylcobalt X can occur in two ways: either by reaction of a cobalt hydride species with mono-adduct (step 5), or directly from the cobalt complex XI without dissociation of the mono-adduct (step 6).

Evidence supporting the intermediacy of the mono-adducts in the production of the di-adduct comes from the variation of yields of mono- and di-adducts with time, when triphenyl phosphite is added (Table 6). This is the only case when such data are available. After 2 h at 80°C, the yield of mono-adducts is 44% (with respect to the amount of starting silane), whereas after 5 h at 80°C it is 31%. The yields of di-adduct are 17 and 41%, respectively. We conclude that the mono-adducts I and II are formed in the early stages of the reaction and are further hydrosilylated to give the di-adduct causing the amount of butenylsilyl derivatives to drop. This

obviously implies that di-hydrosilylation of a diene is a stepwise process. Our results will be interpreted in terms of such a consecutive pathway.

The increasing tendency favouring mono-adducts, as the initial diene/silane ratio *is* increased (Table 2), is easily explained. After the mono-adduct has been formed and displaced from the cobalt complex, there is competition between diene molecules and the olefins (i.e., mono-adducts); increasing the amount of diene competing for a fixed quantity of cobalt complex decreases the chances of coordination of the olefin and thus the amount of di-adduct formed decreases as the diene/silane ratio increases.

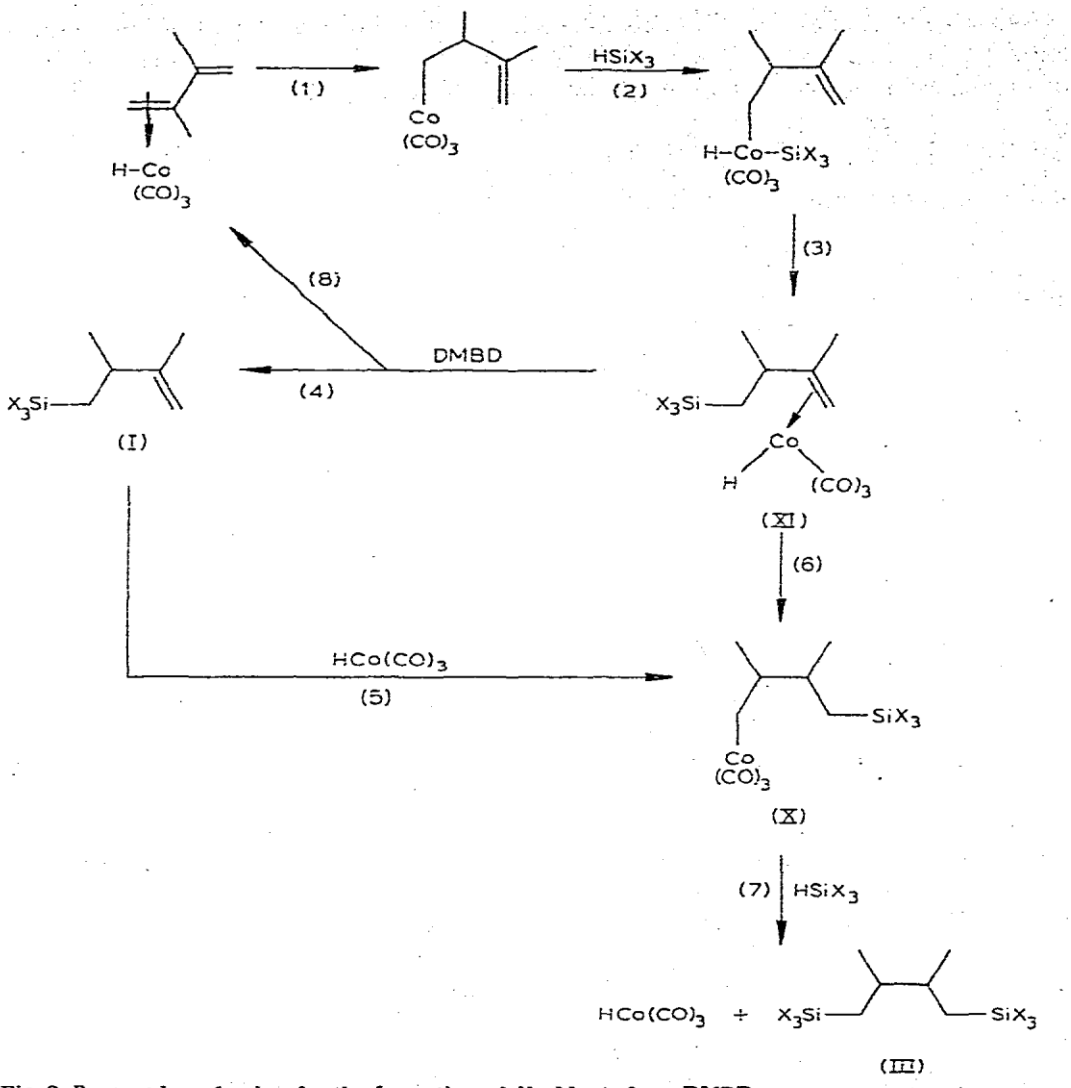


Fig. 2. Proposed mechanism for the formation of di-adducts from DMBD.

TABLE 6

HYDROSILYLATION OF DMBD CATALYSED BY $[Co_2(CO)_8]$: VARIATION OF LIGAND [a]

Ligand [b]	Time (h)	Yield (%) [c]	Ratio of silane used in forming mono-adducts to that used in di-adduct formation	Ratio of 1,2- to 1,4-monoadducts
None	4	69	54/46	60/40
PPh_3	2	93	77/23	55/45
$P(o\text{-}CH_3C_6H_4)_3$	2	45	69/31	65/35
PMe_2Ph	2	69	75/25	50/50
$P(OPh)_3$	2	65	67/33	60/40
$P(OPh)_3$	5	90	46/54	60/40

[a] DMBD, 8.8 mmol; $HSi(OSiMe_3)_2Me$, 4.4 mmol; $[Co_2(CO)_8]$, 6.8×10^{-2}; 80°C. [b] L/CO, 1; added as benzene solutions. [c] Based on silane; calculated by quantitative GLC.

The decrease in the formation of di-adducts as the temperature rises (Table 4) is probably due to the relative thermal instability of the cobalt—mono-olefin bond in the intermediates compared to the cobalt—diene bond. Hydrosilylation of olefins by $[Co_2(C0)_8]$ at temperatures above 60°C, leads to decomposition of the catalyst and

low yields [8]. Thus the overall yield of hydrosilylated products from the $[Co_2(C0)_8]$-catalysed reaction between DMBD and $HSi(OSiMe_3)_2Me$ drops from 93 to 69% upon increasing the temperature from 60-80°C (reaction time 4 h). However, the yield of mono-adducts (with respect to starting silane) is 38% at 60°C and 37% at 80°C. The drop in overall yield is due to the yield of di-adducts falling from 48 to 32% upon increasing the temperature.

The addition of a phosphine or phosphite ligand causes an increase in the amount of mono-adduct formed. This may be due to increasing difficulty in coordinating the sterically hindered mono-adduct olefin II, due to the replacement of a carbon monoxide ligand by a more bulky phosphine or Phosphite ligand.

The addition of polar solvents favours the formation of mono-adducts_(Table 5). This effect has already been considered (see Results section).

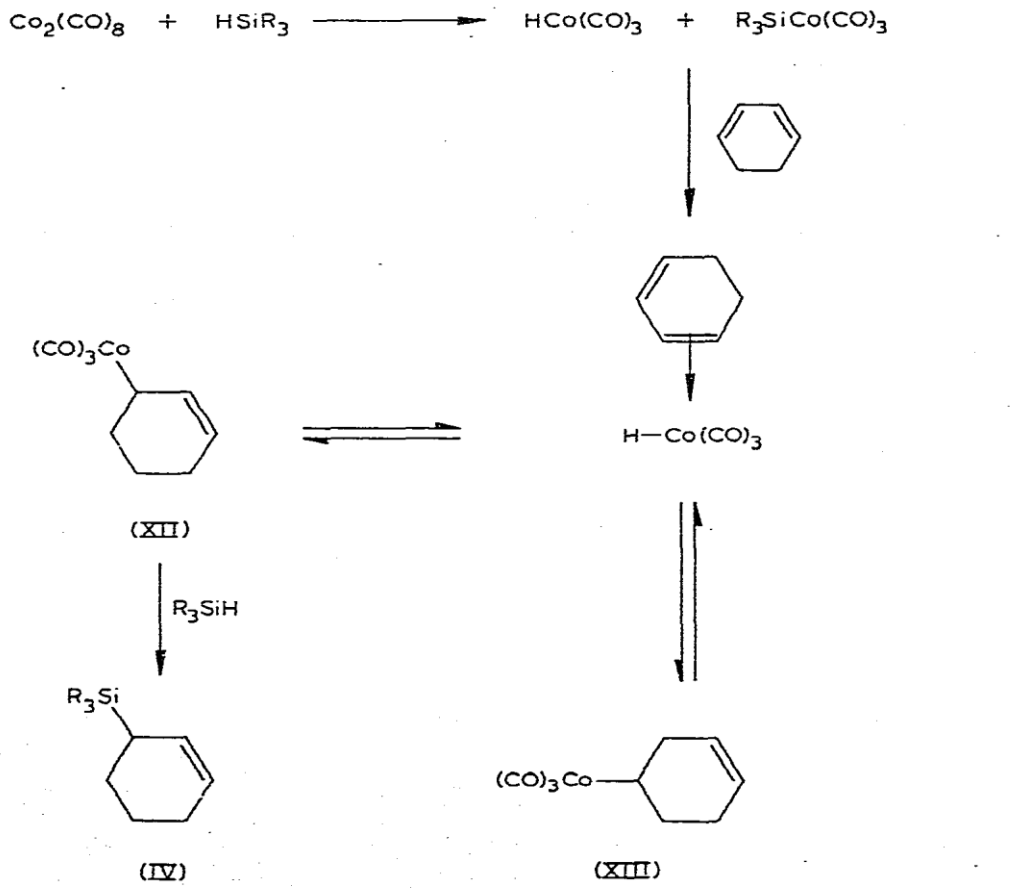


Fig. 3. Proposed mechanism for the formation of 2-cyclohexenylsilanes from 1,3-cyclohexadiene.

Doubling the amount of catalyst from 1 mol% to 2 mol%, relative to silane (from 0.5 mol% to 1 mol% relative to diene) should lead to a small increase in the amount of di-adduct formed. However, a small decrease is observed (Table 3). It may be that the small differences such a change would cause are within the limits of experimental error.

II. The hydrosilylation of cyclic dienes

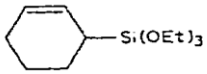
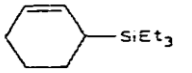
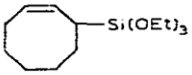
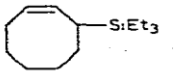
It is to be expected that the mechanism for cyclic dienes (shown in Fig. 3 for 1,3-cyclohexadiene) is in principle similar to that for acyclic compounds. Thus, the first step is envisaged as the binding of the diene and the hydridocobalt(I) species. Subsequent insertion may give either of the possible secondary cycloalkenylcobalt complexes XII or XIII. The σ-alkenylcobalt complex XII is likely to be more stable than its isomer XIII and thermodynamic control thus explains the formation exclusively of the hydrosilylated product IV derived from XII.

In the hydrosilylation of 1,4-cyclohexadiene it is likely that initial isomerisation occurs followed by hydrosilylation and that isomerisation is rate-limiting.

Experimental

All reactions were carried out under pure argon, using freshly distilled, dry, degassed solvents.

^{1}H NMR spectra were recorded on a Varian Associates A60 or T60 spectrometer. IR spectra were obtained with a Perkin—Elmer 457 grating spectrophotometer as thin films. Mass spectrum—GLC analyses were carried out on a machine constructed from an Edwards E606 Fast Scanning Mass Spectrometer and a Pye-Unicam Model 104 Series 64 gas chromatograph. Preparative GLC separations were carried out using a Pye-Unicam. Model 105 preparative GLC. The GLC analysis of the reaction products was carried out on a Pye Series 104 gas chromatograph, using a 6 ft column of 10% SE30 on 100-120 mesh Chromasorb G, using the following conditions:

Compound	Temp (°C)	Internal ref.
$(Me_2)C{=}C(Me)CH_2SiEt_2Me$	160	Indane
$CH_2{=}C(Me)CH(Me)CH_2SiEt_2Me$	160	Indane
$(Me_2)C{=}C(Me)CH_2Si(OSiMe_3)_2Me$	165	Indane
$CH_2{=}C(Me)CH(Me)CH_2Si(OSiMe_3)_2Me$	165	Indane
$[CH(Me)CH_2Si(OSiMe_3)_2Me]_2$	215	Diethyl phthalate
	165	Indane
	140	Indane
	230	Indane
	170	Indane

All the unsaturated organic compounds were commercial products, dried over molecular sieves and distilled in an inert atmosphere prior to use, with the exception of 2,3-dimethy1-1,3-butadiene which was prepared by the literature method [18]. Triethoxy- [19], triethyl- [20], diethylmethyl- [21], and bis(trimethylsiloxy)methyl-silanes [22] were prepared by standard methods. Octacarbonyldicobalt(0) in toluene and the ligands were commercial samples.

TABLE 7

^{1}H NMR DATA FOR $CH_2{=}C(CH_3)CH_A[C(H_B)_3]C(H_C)_2SiX_3$ [a,b]

Chemical shift (τ, ppm) (integration, description)	Assignment (coupling constant)
5.3—5.5 (2 H, broad multiplet)	$CH_2{=}C{-}$
7.7—8.0 (1 H, broad multiplet)	$C{=}C{-}CH{-}C$
8.4 (3 H, broad singlet)	$C{=}C{-}CH_3$
9.07 (3 H, broad doublet)	$C{-}C{-}CH_3(J_{AB}$ 7 Hz)
9.50 (2 H, broad doublet)	$C{-}C{-}CH_2{-}Si(J_{AC}$ 5 Hz)
10.00 (18 H, singlet)	$Si{-}O{-}Si{-}CH_3$
10.08 (3 H, singlet)	$Si{-}CH_3$

[a] Data for Ia only; the ^{1}H NMR of Ib is similar, but most resonances are obscured by the ethylsilyl resonances. [b] 60 MHz spectra; CCl_4 solution; benzene reference.

Hydrosilylation of 2,3-dimethyl-1,3-butadiene by bis(trimethylsiloxy)methylsilane catalysed by octacarbonyldicobalt(0)

A typical procedure for the hydrosilylation of 1,3-dienes is as follows. Octacarbonyldicobalt(0) (0.34 g, 1.0 mmol) was added to a mixture of 2,3-dimethyl1,3-butadiene (2.87 g, 35 mmol) and bis(trimethylsiloxy)-methylsilane (3.90 g, 18 mmol) at room temperature. The mixture was stirred at room temperature for 8 h. After 1 h an exothermic reaction ensued, necessitating further cooling. Volatiles were removed under reduced pressure (2 mmHg) and distillation yielded the 1/1 diene/silane adducts (1.2 g, 23%), b.p. 94°C/8 mmHg. (Found: C, 51.1; H, 10.9. $C_{12}H_{32}O_2Si$ calcd.: C, 51.3; H, 10.6%). Mass spectrum—GLC analysis showed this fraction consisted of two 1/1 diene/silane adducts (P^+ 304). These were separated by preparative GLC and the

lower boiling isomer identified as 2,3-dimethy1-3-butenylbis(trimethylsiloxy)-methylsilane from its ^{1}H NMR spectrum (Table 7). The other isomer was identified as 2,3-dimethy1-2-butenylbis(trimethylsiloxy)methylsilane from its ^{1}H NMR spectrum (Table 8). No carbon—carbon double bond stretching frequency could be observed in the IR spectrum.

TABLE 8

^{1}H NMR DATA FOR $(CH_3)_2C{=}C(CH_3)CH_2SiX_3$ [a]

Compound	$(C\underline{H}_3)_2C{=}C(C\underline{H}_3)C$ [b]	$C{=}C{-}C\underline{H}_2{-}Si$ [c]	SiX_3
IIa	8.45	8.62	10.00 (18 H, singlet, $-Si-O-Si-CH_3$)· 10.11 (3 H, singlet, $-Si-CH_3$)
IIb	8.40	8.50	9.0-9.6 (10 H, $SiCH_2-CH_3$) 10.03 (3 H, $Si-CH_3$)

[a] 60 MHz spectra; CCl_4 solution; benzene reference. [b] Chemical shift, τ, ppm; 9 H, singlet. [c] Chemical shift, τ, ppm; 2 H, singlet.

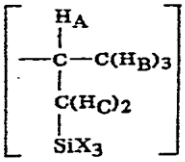
Further distillation of the reaction mixture yielded the 1/2 diene/silane adduct (1.9 g, 41%), b.p. 90°C/0.05 mmHg. (Found: C, 45.0; H, 9.89. $C_{20}H_{54}O_4Si_6$ calcd.: C, 45.6; 10.3%). This compound was identified as 1,4-bis[bis(trimethylsiloxy)methylsilyl]-2,3-dimethylbutane from its ^{1}H NMR (Table 9).

Hydrosilylation of 2,3-dimethyl-1,3-butadiene by diethylmethylsilane catalysed by octacarbonyldicobalt(0)

This reaction was carried out in an analogous fashion, using 2,3-dimethyl-1,3butadiene (2.87 g, 35 mmol), diethylmethylsilane (1.41 g, 14 mmol) and octacarbonyldicobalt(0) (0.34 g, 1.0 mmol). Distillation, after a removal of excess volatiles, yielded the 1/1 diene/silane adducts (2.0 g, 75%), b.p. 93°C/12 mmHg. (Found: C, 71.4; H, 13.0. $C_{11}11_{24}Si$ calcd.: C, 71.7; H, 13.1%). Mass spectrumGLC analysis showed this fraction consisted of two 1/1 diene/silane adducts (P 184). These were separated by preparative GLC. The lower boiling isomer was identified as 2,3-dimethy1-3-butenyldiethylmethylsilane from its ^{1}H NMR spectrum (Table 7). The other isomer was similarly identified as 2,3-dimethy1-2- butenyldiethylmethylsilane (Table 8).

TABLE 9

^{1}H NMR DATA FOR $X_3SiCH_2CH(CH_3)CH(CH_3)CH_2SiX_3$ [a,b]



Chemical shift (τ, ppm) (integration, description)	Assignment (coupling constant)
8.2—8.7 (2 H, broad multiplet)	C—CH—C
9.17 (6 H, doublet)	$C-CH_3$ (J_{AB} 6.5 Hz)
9.6 (4 H, doublet)	$-C-CH_2-Si$ (J_{AC} 4.0 Hz)
9.92 (36 H, singlet)	$Si-O-Si-CH_3$
10.00 (6 H, singlet)	$Si-CH_3$

[a] $X_3 = (Me_3SiO)_2Me$. [b] 60 MHz, spectra; CCl_4 solution; benzene reference.

Hydrosilylation of cyclic dienes by triethoxysilane catalysed by octacarbonyldicobalt(0)

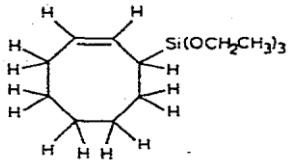
A typical example of the procedure used is that for the hydrosilylation of 1,3- cyclohexadiene.

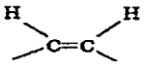
Octacarbonyldicobalt(0) (0.34 g, 1.0 mmol) was added to a mixture of 1,3- cyclohexadiene (3.6 g, 45 mmol) and triethoxysilane (2.26 g, 13.75 mmol) at room temperature. The mixture was stirred at room temperature for 8 h. Distillation, after removal of excess volatiles, yielded 2-cyclohexenyltriethoxysilane (1.75 g, 52%), b.p. 122°C/10 mmHg, identified by its ^{1}H NMR spectrum [1]. (Found: C, 58.8; H, 9.69. $C_{12}H_{24}SiO_3$ calcd.: C, 59.0; H, 9.84%). GLC analysis showed that this contained one adduct only (Table 10).

GLC was used to show that no reaction had occurred in the attempted hydrosilylation of 1,5-cyclooctadiene; and a crystalline solid was formed upon stirring norbornadiene and triethoxysilane in the presence of octacarbonyldicobalt(0).

Other data are summarised in Tables 1-9.

TABLE 10

^{1}H NMR DATA FOR  [a]

Chemical shift (τ, ppm) (Integration, description)	Assignment
	
4.35—4.7 (2 H, multiplet	
6.3 (6 H, quartet)	—OSiCH$_2$—
7.75—9.7 (11 H, broad multiplet)	ring protons
9.9 (9 H, triplet)	—OSi—C—CH$_3$

[a] 60 MHz spectra; CD_2Cl_2 solution, $CHCl_3$ reference.

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